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K. L. Tully and J. E. Hickman contributed equally to this work.

Key Points:

- Agriculture is intensifying across sub-Saharan Africa (SSA) with implications for nitrogen cycling
- Maize yields in Kenya trials were 4.5 times higher than in Tanzania, but yields plateaued with fertilizer additions above 100 kg N ha−1 yr−1
- Fertilizer applications below 50 kg N ha⁻¹ yr⁻¹ did not lead to major losses of nitrogen from maize agroecosystems in SSA

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$\widehat{\mathbf{F}}$ **The Fate of Nitrogen During Agricultural Intensification in East Africa: Nitrogen Budgets in Contrasting Agroecosystems**

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Abstract The intensification of agricultural systems in sub-Saharan Africa (SSA) is necessary to reduce poverty and improve food security, but increased nutrient applications in smallholder systems could have negative consequences for water quality, greenhouse gas emissions, and air quality. We tracked nitrogen (N) inputs and measured maize (*Zea mays*) biomass, grain yields, N leaching, and nitric oxide (NO) and nitrous oxide fluxes from a clayey soil in Yala, Kenya and a sandy soil in Tumbi, Tanzania, with application rates of 0, 50, 75, 100, 150, and 200 kg N ha−1 yr−1 over two cropping seasons. Maize yields were 4.5 times higher in Yala than Tumbi, but yields plateaued at both sites with fertilizer applications at or above 100 kg N ha⁻¹ yr⁻¹. Partial N budgets in Yala were typically negative, meaning more N was exported in maize biomass plus grain or lost from the system than was added in fertilizer. In Tumbi, N budgets were negative at lower fertilizer levels but positive at higher fertilizer levels. At both sites most (96%) of the N was lost through maize biomass/grain removal and N leaching. Fertilizer additions at or less than 50 kg N ha−1 yr−1 on these two contrasting sites resulted in minor gaseous N losses, and fertilizer additions less than 200 kg N ha−1 yr−1 caused relatively little change to N leaching losses. This indicates that the modest increases in fertilizer use required to improve maize yields will not greatly increase cropland N losses.

Plain Language Summary Crop yields in smallholder agriculture across sub-Saharan Africa are low but could be increased by greater applications of nitrogen fertilizer. However, greater use of nitrogen fertilizer creates potential for higher emissions of nitrogen trace gases and nitrogen leaching losses. This study added nitrogen fertilizer doses (0, 50, 75, 100, 150, and 200 kg of nitrogen per hectare) to maize cropland in two smallholder farming sites, one on clay-rich soils in Kenya and one on sandy soils in Tanzania. It tracked removal of nitrogen fertilizer via harvested maize and losses as nitrous oxide (a greenhouse gas), NO (an air pollutant), and leaching of soil solution. Yields were 4.5 times higher on the clayey soil; yields plateaued at nitrogen application above 100 kg per hectare. Leaching losses far exceeded gaseous losses at both sites: 96% of nitrogen was removed in harvested crops and soil solution. Nitrogen additions at or below 50 kg of nitrogen per hectare led to minor increases in gaseous nitrogen losses and additions less than 200 kg of nitrogen per hectare did not increase soil solution losses. This indicates that the modest increases in fertilizer use required to improve maize yields will not greatly increase cropland nitrogen losses.

1. Introduction

The technological transformations of smallholder agricultural systems that took place as part of the Green Revolution in Asia and Latin America in the second half of the twentieth century have been slow to take hold in sub-Saharan Africa (SSA). A history of low fertilizer use in SSA has led to widespread depletion of soil nitrogen (N) and other nutrients (Cobo et al., [2010;](#page-19-0) Vitousek et al., [2009\)](#page-21-0), limiting crop productivity and contributing to the inability of many smallholders to break out of poverty (Barrett & Bevis, [2015](#page-19-1)). New efforts at agricultural intensification became a focus of international development and national policy in multiple African countries during the 2000s (Jayne & Rashid, [2013;](#page-20-0) Jayne & Sanchez, [2021\)](#page-20-1). Many agricultural development practitioners have focused on restoring soil nutrients, increasing productivity, and alleviating poverty through the intensification of smallholder agriculture (AGRA, [2009\)](#page-19-2). Although there is some debate about the

ability of smallholder agricultural intensification to alleviate poverty in SSA, it is widely seen as critical for reducing food insecurity (Dawson et al., [2016](#page-19-3); Denning et al., [2009;](#page-19-4) Harris & Orr, [2014](#page-19-5); Larson et al., [2018;](#page-20-2) Ollenburger et al., [2019](#page-20-3)). Potential obstacles to smallholder intensification include the cost and availability of fertilizer or improved seed and small or inconsistent yield responses to fertilizer (Burke et al., [2016;](#page-19-6) Denning et al., [2009](#page-19-4); Roobroeck et al., [2021](#page-20-4)). The initial goal of the Abuja Declaration on Participatory Development (1989) was to increase mean fertilizer inputs to 50 kg nutrients ha−1 by 2015 (UN ECA, [1990\)](#page-21-1). This goal was not met (Masso et al., [2017\)](#page-20-5). However, nutrient inputs have increased, and although mineral fertilizer use remains less than 10 kg N ha⁻¹ in most countries in SSA, it has increased to >50 kg N ha⁻¹ in some countries (Jayne & Sanchez, [2021\)](#page-20-1) while inputs from biological N fixation have increased in several others (Elrys et al., [2019\)](#page-19-7).

Intensification of agriculture with increased fertilizer N inputs almost inevitably results in greater losses of N. In temperate croplands, only about half of added N is taken up by crops (Conant et al., [2013](#page-19-8)). Losses of fertilizer N can have cascading effects on ecosystems including emissions of the greenhouse gas nitrous oxide $(N,0)$, emissions of the air pollutant precursors nitric oxide (NO) and ammonia (NH_3), and leaching of nitrate (NO_3^-) to groundwater, with negative impacts on soils, water, and biodiversity (Galloway et al., [2003;](#page-19-9) Tilman et al., [2002](#page-21-2)). Further, climate change is expected to alter rainfall regimes across SSA (Cook et al., [2020](#page-19-10); Palmer et al., [2023](#page-20-6)), which may alter both crop productivity and N fluxes as leaching losses and gaseous emissions are linked to moisture levels and movement in soils.

The fate of fertilizer N in agroecosystems in Africa has not been as widely studied as it has in other parts of the world (Huddell et al., [2020](#page-20-7)). Nitrous oxide emissions range from 1% to 7% of added fertilizer N across other agricultural systems (Bouwman, [1996;](#page-19-11) Bouwman et al., [2002](#page-19-12); Davidson et al., [2008](#page-19-13); Palm et al., [2002](#page-20-8)) and range widely based on precipitation and soil texture. Recent work suggests that emissions of fertilizer-induced N2O tend to be lower in Africa than in other parts of the world—often considerably less than 1% of added fertilizer (Hickman et al., [2014](#page-19-14), [2015](#page-19-15); Zheng et al., [2019b\)](#page-21-3)—though the effects of fertilization on other gaseous losses such as NO or $NH₃$ are less well understood (Hickman et al., [2017](#page-19-16); Zheng, Kilasara, et al., [2018](#page-21-4)). Globally, about 15% of applied fertilizer N is estimated to be lost through $NO₃$ ⁻ leaching in maize systems (Zhou & Butterbach-Bahl, [2013\)](#page-21-5). Studies in SSA show leaching losses of roughly 10%–20% of added fertilizer (Kamukondiwa & Bergström, [1994](#page-20-9); Kimetu et al., [2006](#page-20-10); Mapanda et al., [2012;](#page-20-11) Nyamangara et al., [1994\)](#page-20-12), though losses of 5% and 35% have also been observed (Poss & Saragoni, [1992;](#page-20-13) Sogbedji et al., [2000\)](#page-21-6).

Across a series of four papers, Zheng et al. evaluated the response of NH_3 , N_2O , NO_3^- , and crop biomass N to fertilizer additions in sandy and clayey soils in Tanzania, and found that there were tipping points above which N losses increased rapidly without concurrent increases in maize yields (Zheng, Kilasara, et al., [2018;](#page-21-4) Zheng, Mmari, et al., [2018](#page-21-7); Zheng et al., [2019a,](#page-21-8) [2019b\)](#page-21-3). Nitrogen leaching losses tended to be higher in sandy soils, where NO_3^- losses reached as high as 74 kg N ha⁻¹ under fertilization rates of 150 kg N ha⁻¹, though with large inter-annual variation (Zheng et al., [2019a\)](#page-21-8). Quantifying the N losses in response to different fertilizer application rates under different soil and rainfall conditions would help to evaluate the potential environmental impact of the intensification of smallholder agriculture now occurring over wide areas of SSA.

Here, we tracked N losses and removal as N_2O , NO , NO_3 ⁻ leaching at 2 m below the ground surface, and in crop biomass under ranges of fertilizer inputs that simulated intensification in smallholder agriculture at two East African sites that capture the range of climate and soils on which intensification is likely to occur. One site was in western Kenya with clayey soils and high rainfall and the other was in central Tanzania with sandy soils and half as much rainfall as the Kenyan site. We combined tracing of isotopically labeled N fertilizer into crops with data on leached NO_3^- and gaseous N emissions to construct partial N budgets over multiple years and over annual fertilization rates that ranged from 0 to 200 kg N ha⁻¹ yr⁻¹. We aimed to better understand the fate of fertilizer N in intensifying maize agroecosystems and to test current understanding of how intensification will affect the fate of N in African smallholder agriculture over a range of rainfall and soil conditions in which it is likely to occur. We expected the partial N budgets to show: (a) greater NO_3^- -N leaching on the sandier soils despite lower rainfall; (b) relatively low fluxes of $N₂O$ overall, with lower $N₂O$ and higher NO fluxes from the sandier soils; (c) N mining at N application rates of 75 kg N ha⁻¹ yr⁻¹ or less; and (d) exponential growth of N₂O with increasing fertilizer but a leveling off of NO emissions consistent with limitation of nitrifier population growth.

Table 1

Soil Characteristics (0–15 cm) of the Experimental Plots in Yala, Kenya and Tumbi, Tanzania

Note. Data are presented as means across all blocks, with standard error of the mean in parentheses $(n = 4)$. See Tully et al. (2016) (2016) for soil data $(0-400 \text{ cm})$ at the two sites.

a Available P determined by Mehlich 3 extraction.

2. Methods

2.1. Study Sites and Experimental Design

The studies were conducted in two sites with contrasting soil texture, mineralogy, and rainfall: (a) Yala, located in the highlands of western Kenya, has sandy clay loams of oxidic mineralogy (Eutric Ferralsol; 37% clay in top 15 cm); and (b) Tumbi, located in mid-western Tanzania, has loamy fine sand soils of mixed mineralogy and small amounts of oxidic minerals (Ferric Acrisol; 9% clay in top 15 cm) (Table [1\)](#page-2-0). Together, Ferralsols and Acrisols comprise 13% of the total land area in SSA (Dewitte et al., [2013](#page-19-17)). Annual rainfall in Yala, Kenya averages 1,800 mm per year between the *long rains* (March–June) and the *short rains* (October–December), allowing for two cereal crops to be cultivated per year. Tumbi, Tanzania receives about 900 mm per year during one rainy season (November–April), which allows for only cereal one crop per year.

Experimental maize (*Zea mays*) trials were established in January 2011 on land owned by the Kenya Broadcasting Corporation-Nyamninia in Yala, Kenya and in November 2012 at the Tumbi Agricultural Research Institute (ARI) in Tabora, Tanzania. The field site in Yala was converted to agriculture in the 1960s or 1970s. The focal field was left as bush fallow from 1979 to 1989 and again from 1994 to 2007. In other years maize, beans (multiple

genera within the *Fabaceae* family), and sweet potatoes (*Ipomoea batatas*) were cultivated. Tumbi ARI was established in 1975, and the surrounding miombo woodlands were cleared for maize cultivation in 1978. The focal field site was abandoned in 1996 and left grass fallow until 2003. From 2003 to 2004, it was under tobacco (*Nicotiana tabacum*) cultivation, but then left to bush fallow until the field was prepared for the experimental trial in November 2011.

Plots were established at both sites in a randomized complete block design with six levels of inorganic fertilizer (0, 50, 75, 100, 150, and 200 kg N ha⁻¹). One organic treatment (75 kg N⁻¹) was added in Tumbi, applied as chopped leaves from *Gliricidia sepium* (abbreviated as GLIR), a leguminous tree (see Tully et al., [2016](#page-21-9) for full description of organic treatment). In Tumbi, maize was planted in a ridge-furrow system to conserve rainwater, following local practice. In Yala, maize was planted on a flat field following local practice. Hybrid maize varieties were planted at 30 cm in-row spacing by 75 cm between-row spacing (Kenya Seed Company WH403 in Yala and Dekalb 8053 in Tumbi). The plots were 3×6 m (18 m²), with a 0.5-m buffer between each plot in Yala and 1-m buffer between each plot in Tumbi. Eighty maize plants were planted in each plot, and the two outside rows of maize were considered buffer plants. All measurements were taken from randomly selected locations within the central areas of the plots $(10.8 \text{ m}^2; 24 \text{ plants total}; \text{Figure S1 in Supporting Information S1}).$

At both Yala and Tumbi, inorganic fertilizer was applied in a split application: one-third at planting as diammonium phosphate (DAP; 18% N) at ∼5 cm depth with the seed. The remaining two-thirds of fertilizer N was added 5–6 weeks later (maize growth stage V5–6) as urea (46% N) within a 10 cm diameter ring around each maize plant and incorporated into the soil. In Yala, fertilized maize was cultivated during the long rains and unfertilized maize during the short rains. In Tumbi, fertilized maize was grown during the single rainy season and plots were fallowed during the dry season. Four replicate blocks were established, each containing a single plot for each treatment, for a total of 24 plots in Yala and 28 plots in Tumbi.

2.2. Maize Harvest and Yield

Maize plants were harvested in mid to late August in 2011, 2012, and 2013 in Kenya and in late April to early May in 2013 and 2014 in Tumbi. All plants were collected from inside the buffer area (24 plants total; Figure S1 in Supporting Information S1). Total stalks and ears were counted and weighed in the field using a hanging scale. Subsamples of grain, stalks, and shelled cobs were collected and weighed fresh within 24 hr of sampling on an analytical balance. These subsamples were then oven-dried at 60°C for 48 hr and re-weighed to determine moisture content. The dry:fresh ratio and number of ears per plot were used to calculate the harvested dry weight in each plot (Hickman et al., [2015;](#page-19-15) Tully et al., [2016](#page-21-9)). Dried subsamples of grain, cobs, and stalks were ground to

pass through a 2-mm mesh and analyzed for total C and N content using elemental analysis (Flash 2000 Series, Thermo Fisher Scientific, Waltham, MA). Nitrogen concentrations in maize tissues were used to calculate the quantity of N exported by harvested grain, cobs, and stover.

As defined in Congreves et al. ([2021\)](#page-19-18), the agronomic efficiency of N (AE-N) in maize was calculated as:

$$
AE - N = (Y_F - Y_C) / Fappl
$$
 (1)

where Y_F and Y_C refer to mean maize grain yields (in kg ha⁻¹) in the treatment where N has been applied and the unfertilized plot, respectively, and F_{appl} is the amount of fertilizer N applied (in kg N ha⁻¹).

As defined in Congreves et al. ([2021\)](#page-19-18), the maize fertilizer-N recovery efficiency was calculated as:

Maize fertilizer – N recovery efficiency (%) = $[(BN_F - BN_C)/F_{appl}] * 100$ (2)

where BN_F and BN_C refer to mean total biomass N (in kg N ha⁻¹) in the treatment where N has been applied and the unfertilized plot, respectively, and F_{appl} is the amount of fertilizer N applied (in kg N ha⁻¹). Total maize biomass N was the sum of N (in kg ha⁻¹) in maize grain, cores, and stover.

As AE-N and fertilizer-N recovery efficiency were calculated annually (using all replicate plot data), we tested the effect of fertilizer treatment with analysis of variance using annual data at Yala and Tumbi using the *lme4* package (Bates et al., [2023](#page-19-19)). Tukey *post-hoc* tests were used to perform pair-wise comparisons among fertilizer levels with the *multcomp* package (Hothorn et al., [2023\)](#page-20-14). Analysis was performed in the R statistical environment (R Core Team, [2020\)](#page-20-15).

2.3. Soil and Water Collection and Analysis

Tension lysimeters (SoilMoisture Corp., Goleta, CA, USA; inner diameter of 4.2 cm) were installed in January of 2012 to collect soil solution in plots receiving 0, 50, 75, and 200 kg N ha−1 (and the organic treatment in Tumbi) from all four replicate blocks. Lysimeters were placed within 15 cm of a maize plant at 15, 120, and 200 cm depth in Yala and at 50, 120, and 200 cm depth in Tumbi in November of 2012 (Tully & Weil, [2014](#page-21-10); Figure S1 in Supporting Information S1). Leaching flux data from Yala in 2012 and 2013 were reported originally in Russo et al. ([2017\)](#page-20-16). All leaching flux data from Tumbi are reported for the first time here.

Lysimeters were purged of any water the day before sampling and a hand pump was used to apply an internal pressure of −0.05 to −0.06 MPa. Soil solutions were collected prior to maize planting to serve as a baseline. Soil solution sampling was conducted daily following maize planting and fertilizer applications and at regular intervals throughout the growing season following precipitation events that were likely to lead to solution flux. Sixty-one soil solution samples were collected from Yala and 78 soil solution samples from Tumbi across the 2-year measurement period although not every lysimeter produced soil solution at each sampling time. The sandy soils of Tumbi had lower soil moisture content $(5\%-10\%)$ than the clayey soils of Yala (30%) and, therefore, the shallow lysimeters were installed at a deeper depth (50 cm) to ensure good contact with the soil. Even so, the coarse soil texture at Tumbi made it difficult for tension to be maintained in many of the lysimeters. As a consequence, estimates of NO₃[−] leaching for the *Gliricidia*, 50, and 75 kg N ha⁻¹ treatments are each based on observations from a single plot, and estimates of leaching from the 0 and 200 kg N ha−1 treatments are based on observations from two plots.

Soil solution samples were preserved in acid-washed (5% HCl) high-density polyethylene bottles to which a pinch of Thymol (5-methyl-2-[1-methylethyl]phenol) was added to inhibit biological activity. Unfiltered water samples were analyzed for NO₃⁻ using an ion-selective electrode (ISE; Horiba, Inc. B-342; Kyoto, Japan) within 3 days of sample collection. Each sample was analyzed three times with the mean reported. The ISE was calibrated every 10 samples using a two-point calibration (6.8 and 68 mg NO_3^- -N L⁻¹), which has high agreement ($r^2 = 0.96$) with the cadmium-reduction colorimetric method for NO_3^- -N analysis (Tully & Weil, [2014\)](#page-21-10). All soil solution samples were transported to the Marine Biological Laboratory (Woods Hole, MA, USA) and samples that exceeded the range of the ISE (>70 mg NO_3^- -N L⁻¹) were analyzed on a LACHAT QuikChem (LACHAT Instruments, Loveland, CO, USA) using the cadmium-reduction method. Soil solutions were diluted if they exceeded the highest calibration standard that was within the detectible range of the colorimeter.

Subsets of soil water solution samples from both Yala and Tumbi were analyzed for NH_4^+ -N in extracts using the indophenol-blue method (Solorzano, [1969\)](#page-21-11) and a spectrophotometer at 640 nm (Shimadzu UV-1601, Kyoto,

Japan). It was determined that NH₄⁺-N concentrations in water samples were between 0.0001% and 2% of NO₃⁻-N concentrations and thus, the study focuses on NO₃⁻-N concentrations as the primary soluble N ion leaving the system. To systematically classify outlier measurements, samples for each replicate N fertilizer treatment plot were evaluated using the Kolmogorov–Smirnov test, a nonparametric test of the null hypothesis that two sample sets come from the same distribution. If the measurements from a single plot were significantly different $(p < 0.01)$ from two or more of the replicate plots, then the measurements from the outlier plot were assumed to be influenced by an uncontrolled variable (e.g., subsurface heterogeneity, biotic influences, or equipment installation errors) and were not included in calculations of the treatment averages (Weihermüller et al., [2007](#page-21-12)). To determine if $NO₃⁻-N$ concentrations differed by fertilization rate, we used a linear mixed effects model with fertilizer rate as the main effect and block as a random effect (*lme4*; Bates et al., [2023\)](#page-19-19). We examined soil solu tion NO₃[−]-N concentrations at 120 and 200 cm separately. As necessary, we used a Box Cox transformation to normalize the concentration data (Box & Cox, [1964](#page-19-20)). Statistics were performed in the R statistical environment (R Core Team, [2020\)](#page-20-15).

2.4. Leaching Flux Model

Infiltration fluid flow through variably saturated soils was calculated using an open-source numerical model called VS2D (Lappala et al., [1987\)](#page-20-17). The model uses a finite difference method to approximate fluid flow based on the Richards Equation. Soil texture measurements were used to parameterize the 5 m deep, 1-D model domain, with a gravity drain boundary at depth. Surface boundary conditions were determined using measured daily total precipitation and calculated evapotranspiration. The unsaturated fluid flow parameters were calibrated using in situ soil moisture time series from 120 to 200 cm below ground surface (Acclima, Inc. Meridian, Idaho, USA). Daily simulation outputs for the study period for observation points (120 and 200 cm) included soil moisture content and vertical fluid velocity.

Modeled soil moisture content and vertical fluid velocity were combined with NO₃⁻-N nutrient concentration measurements to calculate NO₃⁻-N soil solution flux over the study period. Because lysimeters were at 2 m depth, these fluxes represent movement to this depth and are not the equivalent watershed $NO₃⁻-N$ losses because they do not incorporate processes at deeper soil depths. Daily downward fluid flux, q_t (m d⁻¹) was calculated as the simulated daily downward fluid velocity v_t (m d⁻¹) multiplied by the daily soil moisture content, θ_t (Equation [3](#page-4-0)). Daily vertical NO_3^- -N flux, F_t (kg NO_3^- -N ha⁻¹ d⁻¹), was the calculated as the daily fluid flux multiplied by the measured (or interpolated) NO_3^- -N concentration (mg L⁻¹) (Equations [3](#page-4-0) and [4\)](#page-4-1).

$$
q_t = v_t \theta_t \tag{3}
$$

$$
F_{t} = 10q_{t}\left(C_{i} + \left(\frac{C_{i} - C_{i+1}}{m_{i+1} - m_{i}}\right)(m_{i} - t)\right)
$$
\n(4)

where F_t is NO₃⁻-N flux on day *t*, C_i is NO₃⁻-N concentration for measurement *i*, and m_i is the day (*t*) of the most recent previous concentration measurement. If day t has a concentration measurement, then $t = m_i$, and the equation reduces to $F_t = 10q_t(C_i)$. The fluxes reported were calculated from the mean NO₃⁻-N concentration value from the replicate plots of each N fertilizer application rate. The fluid transport model and nutrient flux calculation methods for Yala are found in Russo et al. ([2017\)](#page-20-16). This model and calculations were also used for Tumbi.

2.5. Gas Collection and Analysis

Fluxes of NO and N₂O were measured using round 25.5 cm-diameter polyvinyl chloride (PVC) chambers, which did not include internal fans. When covered and sealed, chamber heights ranged from 8 to 12 cm, producing chamber volumes ranging from ∼4 to ∼6 L. To capture fluxes related to the application of fertilizer, each PVC chamber was centered over a seeding hole at planting; it remained in this position until the second fertilizer application (Figure S1 in Supporting Information S1). Just before the second fertilizer application was made, each chamber was repositioned from its location centered over the plant to an adjacent position between two maize plants within the row (Figure S1 in Supporting Information S1). The chambers remained in this position until the end of the measurement period. Each chamber was positioned to cover soil to which fertilizer was applied at the rate calculated for a single plant for a given treatment. In each block, one additional chamber was inserted between maize rows to quantify fluxes from soils to which no fertilizer was directly applied. In Yala,

the additional chambers were inserted between maize rows in a randomly selected plot in 2011, and in two 0 kg N ha−1 and two 200 kg N ha−1 plots in 2012. In Tumbi, the additional chambers were inserted in between maize rows in two 0 kg N ha⁻¹ and two 200 kg N ha⁻¹ plots in both years of measurements. Statistical analyses suggest that gas fluxes measured from the between-row chambers did not differ by fertilizer treatment ($p > 0.05$), and they were considered representative of fluxes from soils between maize rows for all plots.

2.5.1. Nitric Oxide

In Yala, NO flux measurements were made between 25 March and 31 May in 2011 (dates reported in Table S1 in Supporting Information S1; Hickman et al., [2017\)](#page-19-16). Measurements were made on at least five of the first 7 days following fertilizer applications and were made at least once per week over the rest of the measurement period. The NO measurement period in Yala extended to 4–5 weeks following the second fertilizer application; at this time, fluxes from fertilized plots remained elevated relative to the control. In Tumbi, NO measurements were conducted between 10 December 2012 and 4 April 2013, with higher frequency sampling during the week after fertilizer applications in December and January (dates reported in Table S1 in Supporting Information S1). Fluxes were also elevated at the end of the measurement period, 2 months after topdressing applications. Data on NO fluxes from Yala were originally reported in Hickman et al. [\(2017](#page-19-16)). The NO flux data from Tumbi are reported for the first time here.

NO was measured with a portable chemiluminescent detector (Unisearch Associates LMA-3D, Concord, Ontario, Canada). Flow-through chambers were used, which were fitted with two Swagelok ports. The LMA-3D sampled air by drawing it through Teflon-coated tubing attached to one port. Ambient air scrubbed of NO_x was drawn into the second port through Teflon-coated tubing connected to a column filled with Purafil. At the start of each flux measurement, initial $NO₂$ concentrations in the chamber were measured. Then sample gas was passed through a CrO₃ filter to convert all NO to NO₂, providing measurements of NO_x concentrations. The NO_x concentration was measured at 15 s intervals for 5 min, at which time the $C₁$ filter was taken off-line, and the final NO₂ concentration was measured. The initial and final NO₂ concentrations were used to calculate the linear change in NO₂ concentration within the chamber over time. The change in NO concentration over time was calculated by subtracting the change in $NO₂$ concentration from the change in NO_x concentration.

In addition, fluxes were also corrected for the effects of pressure, temperature, chamber volume, and changes in the N oxide mixing ratio (Hall et al., [2008](#page-19-21)). Specifically, fluxes were calculated as:

$$
F_{\rm NO} = \frac{dC}{dt} \frac{V}{A} + C_A \frac{Q}{A} \tag{5}
$$

where F_{NQ} is the NO flux, dC/dt is the measured rate of NO concentration change in a linear regression, *V* is the chamber volume, A is the surface area of soil covered by the chamber, C_A is the mean NO concentration in the chamber over the measurement period, and *Q* is the flow rate of air through the chamber.

Standard curves were generated immediately before, during, and immediately after each day's flux measurements using a portable cylinder of standard gas with a known NO concentration (0.0992 ppm; Scott-Marin Co., Riverside, CA, USA). Coupled rotameters were used to mix the NO standard gas with ambient air scrubbed of ambient NO_x by a Purafil column to produce 11 different NO concentrations for production of the standard curves. The linear relationship between the LMA-3D detector readings (mV) and standard gas concentration (ppb) was used to calculate chamber NO_x concentrations, accounting for any drift in readings between standard curves; drift was assumed to be linear.

2.5.2. Nitrous Oxide

N2O measurements in Yala were collected from 25 March 2011 to 15 July 2011 and from 6 April 2012 to 21 January 2013 using static chambers (Hickman et al., [2015](#page-19-15)). Samples were collected multiple times during the week following each fertilizer application, once per week for the following 3 weeks, and then more infrequently; a total of 21 measurements were made in 2011 and 2019 measurements were made in 2012–2013 (dates reported in Table S1 in Supporting Information S1). A similar approach was taken in Tumbi, with measurements taken between 10 December 2012 and 26 September 2013, and between 12 December 2013 and 22 April 2014 (dates reported in Table S1 in Supporting Information S1). Data on N₂O fluxes from Yala were originally reported in Hickman et al. (2015) (2015) . The N₂O flux data from Tumbi are reported for the first time here.

Sampling for N₂O was conducted between 8:00 a.m. and 1:00 p.m. Variation in environmental variables over this time may have contributed to variation in the flux measurements and could potentially influence estimates of cumulative N2O emissions. However, measurements for all treatments in a single block were conducted simultaneously to prevent variation in the environment from being confounded with fertilizer treatments. At each sampling time, the PVC chambers were fitted with a lid containing a vent and a sampling port. Twelve mL gas samples were taken using polypropylene syringes at 0, 10, 20, and 30 min after the lid was made air-tight; samples were immediately transferred to evacuated 9 mL crimp top glass vials (Teledyne Tekmar, Mason, OH, USA). Samples were analyzed for N₂O by gas chromatography on a Shimadzu GC-14 gas chromatograph fitted with an electron capture detector (Shimadzu Scientific Instruments, Columbia, MD, USA) at the Cary Institute of Ecosystem Studies in Millbrook, NY, USA. Vials were returned to ambient air pressure by venting excess sample gas immediately before analysis. The Shimadzu $GC-14$ is capable of detecting ambient levels of N₂O, with a detection limit of 0.0678 ppm. Standard curves for gas analyses had a coefficient of determination of at least 0.99. Vials filled with a standard N₂O concentration were added to the sample runs to monitor any possible detection error. Fluxes were estimated by linear regression of the change in concentration over the 30-min sampling period. Individual points were removed from these regressions when they were more than six times higher or lower than the other three time points or if they diverged from a clear trend in the other three points. This procedure was implemented to avoid potentially spuriously high fluxes based on non-significant regressions. Non-significant regressions were used in flux calculations to avoid biasing the statistical distribution of rates by setting all non-significant regressions to zero.

The $N₂O$ flux was determined and fluxes corrected for temperature and pressure as follows:

$$
F_{\text{N}_2\text{O}} = \frac{(b * V_{\text{Ch}} * p * \text{MW}_{\text{N}_2\text{O}} * 60 * 10^3)}{R * T * A_{\text{Ch}}}
$$
(6)

where F_{N_2O} is the N₂O flux (ng N₂O-N cm⁻² h⁻¹), *b* is the change in the mixing ratio of N₂O in the chamber air (ppmv min⁻¹), V_{Ch} is the chamber volume (L), p is the pressure (atm), $MW_{\text{N_2O-N}}$ is the molecular weight of N₂O-N (28.0134 g mol⁻¹), *R* is the gas constant (0.08206 (L * atm)/(K * mol)), *T* is the temperature (°K), and A_{ch} is the chamber base area $\text{(cm}^2\text{)}$.

Cumulative emissions represent the total emissions over a given period of time. Cumulative emissions were estimated by summing linearly interpolated daily fluxes and were used to derive mean daily fluxes. Field-scale emissions were estimated using a weighted average of cumulative fluxes from chambers placed within rows (either over or between plants) and chambers placed between rows:

Cumulative field – scale emissions_i =
$$
\sum_{k=1}^{l} (0.227 \text{(chamberkl)} + 0.773 \text{ (between – row chamberl)})/N
$$
 (7)

where chamber_k is the flux (g N ha⁻¹) from the chamber placed in the *k*th fertilizer treatment (or the control) and *l*th block, between-row chamber_{*l*} is the flux (g N ha^{−1}) from the chamber placed between rows in the *l*th block, and where *n* is the number of replicate blocks. The proportion of the field allocated to fertilizer-induced emissions (0.227) is equal to the proportion of the field area described by a 12.75 cm radius (the radius of the PVC chamber) extending from the stem of each maize plant. It was assumed that the chambers placed within rows, which covered soil to which fertilizer for one plant was added, captured all $N₂O$ and NO fluxes induced by the added fertilizer. It was additionally assumed that the fluxes measured by chambers placed between rows were representative of emissions from the remaining soil in the plot—that is, soils which had no fertilizer-induced emissions, and which were assumed to represent the remaining 77.3% of the plot area. However, it is possible that fertilizers affected emissions from soils that were not covered by either the within-row or between-row chambers, (Figure S1 in Supporting Information S1), which would result in an underestimate.

2.6. Isotopic Tracer Experiment

To provide additional detail on the fate of the current year's fertilizer application, in April 2012 a ¹⁵N tracer experiment was conducted in the 75 kg N ha−1 plots in Yala. The cost and effort of isotope additions precluded applying the tracer in more treatments or in Tumbi. Before planting, soil samples (0–10 and 10–20 cm) were collected from the plots to determine natural ¹⁵N abundance. Two plants in each of the four replicate plots were

fertilized with 5% atom% 15N-labeled dry urea (one third at planting and the remaining two thirds 5 weeks later). In both cases, the labeled fertilizer was applied in a ring within 10 cm of the plant base. One of the two plants was selected for its proximity to the lysimeter installed at 120 cm. At maize harvest, the two labeled plants and two un-labeled "reference plants" were carefully separated into the seven following tissue types: grain, cobs, husks, stems, leaves, silks/tassels, and roots. The same day as harvest, soil samples (0–15 cm) were collected from within 10 cm of the uprooted labeled and unlabeled plants. Samples were oven-dried (60°C for plants and 105°C for soils) and weighed to determine moisture content. Plant samples were ground in a coffee grinder and soils were ground using a mortar and pestle. Samples were transported to the Marine Biological Laboratory Stable Isotope Laboratory for $\delta^{15}N$ and $\delta^{13}C$ analysis (Europa 20-20 continuous-flow isotope ratio mass spectrometer interfaced with a Europa ANCA-SL elemental analyzer; now supplied by Sercon Ltd., Crewe, Cheshire, UK). The analytical precision based on replicate analyses of isotopically homogeneous international standards is ± 0.1 $\%$ for both δ ¹⁵N and δ ¹³C measurements, and about 1% relative of the %N and %C measurements. Fertilizer use efficiency (FUE) was calculated using the isotope dilution method and fertilizer recovery in the soil and plant tissue.

$$
\% FUE-{}^{15}N = (a * TN)/(f * FertilizerN) * 100
$$
\n(8)

where *a* is the atom% excess (above background) in the maize tissue or soil, *f* is the atom% excess in the fertilizer, TN is the total amount of N (kg ha⁻¹) in the maize tissue or soil, and Fertilizer_N is the amount of fertilizer N applied in kg ha−1 (Hauck & Bremner, [1976\)](#page-19-22). As fertilizer was applied in a 10-cm ring around the focal plants, only about 14% of the total plot area received fertilizer. Thus, the $15N$ fertilizer recovery was area-weighted to the 10 cm radius where fertilizer was applied. Fertilizer N contribution to total maize N uptake (N derived from fertilizer) was calculated by dividing the ¹⁵N atom% excess in aboveground biomass by the ¹⁵N atom% excess of the applied fertilizer. Calculations of annual N losses were independent of the $15N$ tracer.

2.7. Calculation of Partial N Budgets

For both Yala and Tumbi, partial N budgets were calculated for two maize growing seasons of intensive sampling (2012 and 2013; 2013 and 2014, respectively) across each N fertilizer level. Trace gas N losses were the sum of NO and N2O emissions. Trace gas emissions were not measured in 2013 in Yala and NO emissions were not measured in Tumbi in 2014. However, these emissions represented a very small percentage of the N budget, conservatively less than 2% of the added fertilizer N. Nitrate-N leaching losses were the treatment-level mean fluxes. The removal of nitrogen in harvested grain, stover, and cores was examined separately. It is common in East Africa to remove the entire maize plant at harvest as the cores and stover are often fed to livestock (Valbuena et al., [2012\)](#page-21-13).

2.8. Likelihood Analyses

Linear, exponential, quadratic, sigmoid, and step functions describing the response of different components of the partial N budget to N fertilization rates were compared:

$$
Y_k = a + b * N_k \tag{9}
$$

$$
Y_k = a * e^{(b*N_k)} \tag{10}
$$

$$
Y_k = a + b * \mathcal{N}_i + c * \mathcal{N}_k^2 \tag{11}
$$

$$
Y_k = \left(a * b * e^{(c*N_k)}\right) / \left(a + b * \left(e^{(c*N_k)}\right) - 1\right)
$$
\n(12)

$$
Y_k = a \quad \text{for } N < b; \ Y_i = c \quad \text{for } N > b \tag{13}
$$

where Y_k is the mean daily NO and N₂O flux (in ng N cm⁻² hr⁻¹) at the *k*th fertilization rate (N, in kg N ha⁻¹), and where *a*, *b*, and *c* are non-zero constants. Likelihood estimates of the model parameters were determined by simulated annealing using the anneal function in the likelihood R package developed by Murphy [\(2022](#page-20-18)). Model comparison was conducted using Akaike's Information Criterion and likelihood-ratio based r^2 values. Likelihood analysis was performed in the R statistical environment (R Core Team, [2020\)](#page-20-15).

3. Results

3.1. Maize Productivity

Fertilizer additions caused yield responses at both sites. In Yala, maize yields increased from ∼6 t ha−1 to 7.5–9.0 t ha−1 yr−1 and from 6 t ha−1 to 7.4–8.8 t ha−1 yr−1 in unfertilized compared to fertilized plots in 2011 and [2](#page-9-0)012, respectively (Table 2). In Tumbi, maize yields increased from 1 t ha⁻¹ in the unfertilized plots to $2-3$ t ha⁻¹ yr⁻¹ in the fertilized plots in 2013, and from 0.2 t ha⁻¹ yr⁻¹ in unfertilized plots to 0.8–1.4 t ha⁻¹ yr⁻¹ in fertilized plots in 2014 (Table [2\)](#page-9-0).

At both sites, the N harvested in maize biomass (grain, stover, and cores) was higher in fertilized plots, and both yields and biomass N leveled off after N inputs reached 100 kg N ha⁻¹ yr⁻¹ (Table [2;](#page-9-0) Table S2 in Supporting Information S1; Figures [1a,](#page-10-0) [1b,](#page-11-0) 2a, and [2b](#page-11-0)). In Yala, a sigmoidal model provided the best fit of the functional response of maize biomass N to fertilizer N additions in 2011 $(r^2 = 0.47)$; Figure [1a;](#page-10-0) Table S2 in Supporting Information S1). In 2012, the sigmoidal model also provided the best fit $(r^2 = 0.71)$, but it was not statistically different from the quadratic model $(r^2 = 0.70)$; Figure [1b](#page-10-0); Table S2 in Supporting Information S1). In 2013 at Tumbi, the linear, exponential, sigmoidal, and quadratic equations explained the total biomass N response to fertilizer N equally well $(r^2 = 0.30, 0.27, 0.39, \text{ and } 0.36; \text{ Figure 2a}; \text{ Table S2 in Supporting Information S1). In}$ 2014, the linear and the quadratic models explained the total biomass N response equally well $(r^2 = 0.53$ and 0.55; Figure [2b;](#page-11-0) Table S2 in Supporting Information S1).

Although maize yields were about 4.5 times higher in Yala than Tumbi, when normalized by an unfertilized plot, the AE-N were similar at the two sites (Figure S2 in Supporting Information S1). The highest AE-N (kg (kg N)^{−1}) was observed in the plots receiving 50 kg N ha⁻¹ yr^{−1} in both Yala (25.8 kg (kg N)^{−1}) and Tumbi (27.7 kg (kg N)^{−1}). The lowest AE-N was observed in plots receiving 200 kg N ha^{−1} in Yala (8.5 kg (kg N)^{−1}) and plots receiving 150 kg N ha^{−1} in Tumbi (4.7 kg (kg N)^{−1}). We found that the AE-N was significantly higher in the plots receiving 100 kg N ha−1 yr−1 or less compared to the higher rates at both Yala and Tumbi (*p* = 0.010 and *p* = 0.05, respectively; Figure S2 in Supporting Information S1).

The total maize biomass fertilizer-N recovery efficiency tended to be higher in Yala than in Tumbi (Figure S2 in Supporting Information S1). While maize fertilizer-N recovery efficiency tended to be higher at lower fertilizer application rates, this relationship was not significant in Yala (Figure S2 in Supporting Information S1). In Tumbi, there was a significant effect of fertilizer application rate on maize fertilizer-N recovery efficiency ($p = 0.036$; Figure S2 in Supporting Information S1). The maize fertilizer-N recovery efficiency was marginally higher in the 50 kg N plot compared to plots receiving 75 kg N as *Gliricidia* (GLIR) or 150 kg N as inorganic fertilizer.

3.2. Isotope Tracer Study

In the 2012 harvest a Yala we observed that about 70% of the ¹⁵N was recovered in maize tissues (nearly 46%) in maize grains alone). This agreed with the 78% N uptake efficiency calculated when we estimated the percent of fertilizer *N* recovered in total maize biomass (e.g., grain, stems, leaves, husks, cores, silk/tassels, and roots; Table [3\)](#page-12-0). We found that about 9% of the ¹⁵N-labeled fertilizer remained in the soil (to 15 cm) after maize harvest (Table [3\)](#page-12-0).

3.3. Gaseous N Losses

Gaseous losses of N₂O and NO were low in both Yala and Tumbi—the two gases combined represented less than 1% of added N across all fertilization levels (Table [4;](#page-13-0) Figure [3](#page-14-0)). Emissions of both gases increased during the period following fertilizer applications and remained elevated for several weeks in Yala (Figures S3 and S4 in Supporting Information S1). NO fluxes also increased following fertilization in Tumbi, but returned to background levels within a week. N2O emissions also increased following fertilization in Yala in both years and in Tumbi in 2013, but generally peaked and declined over the course of one to 2 weeks in Yala, and more quickly in Tumbi (Figures S3 and S4 in Supporting Information S1). In 2014, fertilization had almost no effect on N₂O emissions in Tumbi; NO was not measured in that year.

Emissions at Yala, and to a lesser extent Tumbi, could be described as mathematical functions of N input rate, though the patterns differed between the two gases, and there was some variation between sites. In Yala, NO

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Figure 1. Relationship between inorganic fertilizer N input rate and loss or removal pathways from experimental maize plots for 3 years in Yala, Kenya. Biomass N (a, b) includes N in grain, stover, and cobs. NO₃⁻ losses in panel (g) refer to leaching below 2 m. Gray squares indicate 2011 measurements, open circles indicate 2012 measurements, and gray triangles indicate 2013 measurements; error bars represent the standard error of the mean. The black solid line depicts the linear model, the red solid line depicts the exponential model, the blue dashed line depicts the sigmoidal model, and the purple solid line depicts the quadratic model.

Figure 2. Relationship between inorganic fertilizer N input rate and loss or removal pathways from experimental maize plots for 2 years in Tumbi, Tanzania. Biomass N (a, b) includes N in grain, stover, and cobs. Note the large differences in Y axes for panels (c) and (d). NO₃⁻ losses in panels (f) and (g) refer to leaching below 2 m. Gray squares indicate 2011 measurements, open circles indicate 2012 measurements, and gray triangles indicate 2013 measurements; error bars represent the standard error of the mean. The black solid line depicts the linear model, the red solid line depicts the exponential model, the dark blue dashed line depicts the sigmoidal model, the purple solid lide depicts the quadratic model, and the light blue dashed line depicts the step model.

Table 3

Percent of 15N-Labeled Urea Recovered in Plant Tissues (Labeled n = 8; Reference n = 8) and Soils (Labeled n = 8; Reference n = 8) Collected From the 75 kg N ha−1 Treatment in the Yala, Kenya Fertilizer Trials in 2012

Note. Numbers in parentheses are the standard error of the mean.

emissions increased sigmoidally as a function of increasing fertilizer inputs, increasing rapidly when fertilizer rates were between 100 kg N ha−1 and 150 kg N ha−1 yr−1, after which emissions plateaued. The sigmoidal model explained over 67% of variation in NO emissions in 2011 and 57% of the variation in 2012 (Table S2 in Supporting Information S1). In contrast, N₂O emissions increased exponentially in Yala, with the exponential model explaining roughly two-thirds of variation in emissions in 2011 and explaining 50% of the variation in 2012 (Table S2 in Supporting Information S1).

In Tumbi, non-linear models better explained the relationship between fertilization rate and NO emissions in 2012, but it was not possible to differentiate between sigmoidal, exponential, or step functions and each model explained about 30% of the variation in NO fluxes (Table S2 in Supporting Information S1). The linear and exponential models best described the functional response of N_2O emissions to N inputs at Tumbi in 2013, but there was no difference between linear and exponential models in 2014 (Table S2 in Supporting Information S1). Fertilization rate explained relatively little of the variation in N₂O emissions in either year ($r^2 = 0.20$ in 2013 and $r^2 = 0.10{\text -}0.26$) in 2014), and temporal variations in $N₂O$ emissions were considerably muted in 2014 (Figure S4 in Supporting Information S1).

Yields tended to reach a maximum of 100 kg N ha⁻¹ yr⁻¹ at both sites; fertilization rates above 100 kg N ha⁻¹ yr⁻¹ were accompanied by increases in N₂O emissions but not additional yield (Figures [1](#page-10-0) and [2\)](#page-11-0). NO emissions effectively plateaued at fertilization rates of 150 kg N ha⁻¹ yr⁻¹ or higher in Yala and at 50 kg N ha⁻¹ yr⁻¹ or higher in Tumbi; fertilizer applications beyond those rates did not result in higher yield-scaled emissions (Figure [4](#page-15-0)).

3.4. Nitrate Leaching Fluxes

Leaching fluxes of N during the growing season comprised a substantial portion of the partial N budget at both Yala and Tumbi and ranged from 12 to 49 kg NO_3 ⁻N ha⁻¹ season⁻¹ in Yala and from 1 to 83 kg NO_3 ⁻N ha⁻¹ season⁻¹ in Tumbi (Figure [3](#page-14-0); Table [4\)](#page-13-0). At both sites, growing season leaching losses of NO₃⁻-N at the 200 cm depth tended to be largest under N inputs of 200 kg N ha⁻¹ yr⁻¹, but there were no significant relationships between N inputs and fertilization rates, and in Yala there was no significant correlation between inputs and leaching overall. Maize uptake in Yala (even just grain N) always exceeded leaching fluxes, often by as much as 90%. However, in Tumbi leaching losses in 2014 were consistently higher (in all treatments except *gliricidia*) than N exported in combined maize grain, stover, and cores (Figure [3\)](#page-14-0). In Yala, the short rains were accompanied by additional N losses in leachate of 14–32 kg N ha⁻¹ season⁻¹. Therefore, the total flux over the 17-month measurement period (encompassing two long and one short growing season; 1 April 2012 to 31 August 2013 with fertilizer applied in each of the two long rain growing seasons) ranged from 98 to 160 kg N ha−1 yr−1 at 120 cm depth and 53–95 kg N ha⁻¹ yr⁻¹ at 200 cm depth. In Tumbi, it was very dry between rainy seasons, and leaching was essentially zero in all treatments during that period except for the 200 kg N ha^{−1} yr^{−1} treatment where we observed about 17 kg NO_3^- -N lost via leaching between growing seasons 2013 and 2014. There were no significant relationships between N inputs and N leaching loss in Tumbi in either year.

3.5. Effect of N Fertilizer Rate on Soil Solution Nitrate Concentrations

Soil solution NO_3^- -N concentrations ranged from 1.5 to 92 mg NO_3^- -N L⁻¹ across the study period (2012–2013) in Yala and from 0 to 180 mg $NO₃⁻-N L⁻¹$ across the study period (2013 and 2014) in Tumbi (Appendix A in Supporting Information S1; Figures S5 and S6 in Supporting Information S1). Although there was no significant effect of fertilizer rate on leaching, we examined the relationship between solution NO_3 ⁻-N concentrations and fertilizer N rate. In Yala, there was no significant relationship between mean soil solution NO_3^- -N concentrations and N fertilizer levels at any depth across the measurement period. In Tumbi, there was a significant effect of fertilizer treatment on NO_3^- -N concentrations at both the 120 and 200 cm depths across the measurement period $(p < 0.001$ in both cases; Table S3 in Supporting Information S1). Overall, the highest $NO₃⁻-N$ concentrations in Tumbi were observed in the 200 kg N treatment (Table S3 in Supporting Information S1).

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Figure 3. Partial N budget across a range of fertilizer treatments in experimental maize plots in Yala, Kenya (a, b) and Tumbi, Tanzania (c, d). Bar plots represent N removed or lost from the plots, and orange points represent fertilizer N inputs added to each plot. GLIR refers to the *Gliricidia sepium* leaf addition in the Tumbi plots only, which were equivalent to 75 kg N ha−1.

3.6. Overall Partial N Budgets

Overall, N fluxes and maize N uptake were higher in fertilized treatments, though they did not always increase systematically with increasing N inputs. When including stover and cores in addition to maize grain as a pathway of N removal, the partial N budgets in Yala, Kenya were nearly all negative. That is, more N was incorporated into maize biomass or lost to the environment than was added in fertilizer (Figure [3,](#page-14-0) Table [4](#page-13-0)). The one exception was a positive partial budget (+53 kg N ha−1) in the highest fertilizer treatment in 2013. In Tumbi, partial N budgets were negative in the 0 and 50 kg N ha⁻¹ treatments, but positive in both years at intermediate to high levels (75 and 200 kg N ha−1). In 2014, N leaching exceeded grain and stover N in Tumbi, when yields were often less than 1 ton ha−1 (Figure [3,](#page-14-0) Table [4](#page-13-0)). We observed the largest negative partial N budgets—or soil mining—in the unfertilized maize plots in Yala. We observed the highest residual fertilizer N—the largest positive budgets—in high fertilizer treatments at Tumbi. The N removed in maize biomass alone nearly always exceeded the N added in fertilizer in Yala, but this was not the case in Tumbi where yields were considerably lower (Figure [3,](#page-14-0) Table [2](#page-9-0)). Leaching of NO₃⁻-N was about two orders of magnitude higher than NO + N₂O losses at both sites.

4. Discussion

4.1. Maize Uptake and Yields

Our results suggest that precipitation is a first-order control over nitrogen use efficiency (NUE) in maize across both sites. Higher yields and greater plant N uptake were consistent with higher maize yields, higher crop NUE, and greater crop biomass N in locations with higher precipitation (Rufino et al., [2006](#page-20-19); Tully et al., [2016](#page-21-9); Zheng, Mmari, et al., [2018\)](#page-21-7). A maize suitability map accounting for both climate and soil texture also predicted higher yields in Yala than Tumbi (Palm et al., [2017\)](#page-20-20). Compared to other budget components, maize biomass was consistently the largest pathway for N removal from soils in Yala and was either the largest or a substantial portion of the partial N budget in fertilized plots in Tumbi.

The nonlinear relationships between N input rate and crop N uptake at both Yala and Tumbi were similar to the patterns observed in a global meta-analysis (Van Groenigen et al., [2010\)](#page-21-14). This pattern reflected overall crop yield responses that also plateaued at 100 kg N ha⁻¹ yr⁻¹. Many studies have documented a diminishing return

Figure 4. Relationship between yield and loss pathways from experimental maize plots for 2 years in Yala, Kenya (a, c, e) and Tumbi, Tanzania (b, d, f).

function between crop yield and N fertilizer application (Cassman et al., [2003](#page-19-23); Hoben et al., [2011](#page-20-21); McSwiney & Robertson, [2005](#page-20-22)). Our study provides additional evidence that in SSA this occurs at fertilization rates above 100 kg N ha−1 yr−1 (Vanlauwe et al., [2010;](#page-21-15) Zheng, Mmari, et al., [2018\)](#page-21-7).

4.2. Nitrate Leaching

Nitrate losses were much larger than gaseous NO and $N₂O$ losses. Our results showed the interacting effects of precipitation and soil texture on NO_3^- -N leaching losses. Although we expected greater NO_3^- -N leaching from the sandier soils of Tumbi, leaching rates were comparable between the two sites despite large differences in rainfall and soil texture (ranging from 10% to 80% of the fertilizer added). In Yala, NO_3^- -N leaching was influenced by both higher precipitation (double that in Tumbi) and oxidic mineralogy (Roobroeck et al., [2021\)](#page-20-4) in which clay

aggregation creates drainage dynamics similar to sandy soils (Sanchez, [2019\)](#page-20-23). In Tumbi, despite sandy soils, we often were unable to collect water from lysimeters, suggesting that rainfall was insufficient to transport NO_3^- -N deep into the soil column, therefore reducing leaching losses. The influence of precipitation was consistent with the lower leaching in 2013 than in 2012 in Yala, when rainfall amounts, yields, and maize N uptake were all lower than in 2012.

Leaching fluxes of 12–49 kg N ha⁻¹ season⁻¹ in Yala and 83 kg N ha⁻¹ season⁻¹ in Tumbi spanned nearly the entire range of fluxes reported in a review of N leaching in tropical croplands (Huddell et al., [2020](#page-20-7)). Similar large variation was found at another sandy soil site in Tanzania, where NO₃⁻-N leaching was roughly three times larger in a rainy than a dry year, even though yields tended to be smaller in the year with greater precipitation (Zheng et al., [2019a](#page-21-8)). Intra-seasonal rainfall variation may also explain the increased leaching losses in 2014 in Tumbi. If precipitation was insufficient to transport fertilizer N below the rooting zone in 2013, the N retained in the soil over the dry season was available to be leached during the 2014 rainy season and would have led to larger seasonal fluxes below the maize rooting zone. Overall, the quantities of N leaching flux were similar to those reported in Zheng et al. [\(2019a](#page-21-8)) for sandy (6–74 kg N ha⁻¹) and clayey sites (6–26 kg N ha⁻¹) in Tanzanian maize cropland (Table S4 in Supporting Information S1).

We measured soil solution to a depth of 200 cm and considered $NO₃⁻-N$ that leached to below that depth to be lost and not available for plant uptake, but $NO₃⁻-N$ fluxes below this depth do not necessarily translate to high losses to ground water. Soils in these sites are deep and anion exchange sites on the highly weathered clay in Yala may hold NO₃⁻-N in the soil profile and protect it from leaching into lower soil layers (Mekonnen et al., [1997;](#page-20-24) G. Shepherd et al., [2000](#page-20-25)).

4.3. NO and N2O Losses

At both sites, N₂O emissions represented less than 1% of fertilizer N, which was consistent with other studies that have found N₂O emission factors well under 1% in both sandy and clayey soils in Tanzania (Zheng et al., [2019b](#page-21-3)) and Kenya (Hickman et al., 2014 , 2015). We expected higher N₂O emissions from the high rainfall, fine textured soils of Yala than from Tumbi, but surprisingly, N₂O emissions were about twice as large in the first year at Tumbi than in either year at Yala. We propose that most of the $N₂O$ production in Tumbi was the result of nitrification: NO emissions in Tumbi were a factor of 3–6 times larger than in Yala, and NO:N₂O ratios in Tumbi were consist-ently greater than 10:1, consistent with nitrification as the primary source of N₂O (Davidson & Verchot, [2000](#page-19-24)). Nitrification may also have been a major source of N₂O in Yala, where NO:N₂O ratios ranged from roughly 5 to 10:1.

Nitric oxide emissions have been measured much less frequently than $N₂O$ emissions in tropical agroecosystems, resulting in substantial variation in emission factor estimates (Huddell et al., [2020](#page-20-7)). Emissions at our sites were consistent with a global emission factor of less than 1% when fertilization rates are under 200 kg N ha⁻¹ (Bouwman et al., [2002\)](#page-19-12). In addition, NO emissions from the unfertilized treatment were under 0.3 kg N ha⁻¹, which was lower than an estimate of 0.8 kg N ha⁻¹ for tropical agroecosystems (Huddell et al., [2020\)](#page-20-7).

Our NO measurements at both sites did not extend through the entire growing season, and substantial NO emissions can occur during the transition from the dry to the rainy season (Jaeglé et al., [2004\)](#page-20-26). There is new evidence from both Yala and Tumbi that rewetting of dry soil can increase NO fluxes apparently independently of a recent history of fertilizer use (Hickman et al., [2021](#page-19-25)). Artificial wetting experiments in Yala and Tumbi conservatively suggested that a single wetting event was responsible for emissions on the order of 100 g NO-N ha^{−1}, suggesting that hundreds of grams of NO-N ha^{-1} may be emitted each year during these post-wetting pulses.

Relatively small NO and N₂O losses in Yala were likely caused by resource limitation and physical constraints. In Yala, the high yields and high maize biomass N suggested that maize plants outcompeted nitrifying and denitrifying microbes for inorganic N (Groffman & Fisk, [2011](#page-19-26)). The leaching losses of N from topsoil were on the order of tens of kg N ha−1, and likely further reduced the pool of available N. Nitrous oxide emissions are highest when water filled pore space (WFPS) is in an optimal range of roughly $40\% - 80\%$ (Davidson et al., [2000;](#page-19-27) Hickman et al., [2015;](#page-19-15) Millar et al., [2004](#page-20-27)). In Yala, soil water holding capacity was 40% and WFPS was typically between 50% and 65%, suggesting that other limiting factors—such as low availability of NO_3^- or reduced carbon compounds—were likely more important. In the sandy soils of Tumbi, soil oxygen availability may have been a

more important limiting control over denitrification. Water holding capacity in Tumbi was 10% and WFPS was typically around 11% and never higher than 27%, which likely severely limited denitrification.

Our finding of the relationships between N₂O, NO, and N fertilizer have important management implications. As expected, we observed increases in N₂O emissions that were consistent with an exponential response to increasing N application rates at both sites, except in year 2 at Tumbi, suggesting that N stopped being a limiting factor at fertilization rates of 50 kg N ha−1, and that physical factors then limited nitrification, denitrification, or both. Exponential increases in N₂O in response to increasing fertilization are common (Shcherbak et al., [2014](#page-20-28)). When emissions increase exponentially and yield increases are small at high N fertilization, optimizing N inputs can be an important strategy for reducing $N₂O$ emissions.

In contrast to $N₂O$, in both sites, NO emissions followed step-like functions, with rapid increases occurring with any amount of fertilizer addition in Tumbi, and at roughly 75–150 kg N ha⁻¹ in Yala, potentially related to limitations in nitrifier population growth (Hickman et al., [2017\)](#page-19-16). The functional relationship between fertilizer inputs and NO emissions is not well understood, with two studies finding linear relationship (Liu et al., [2005;](#page-20-29) M. F. Shepherd et al., [1991\)](#page-21-16), and one an exponential relationship (Zhao et al., [2015\)](#page-21-17), though none were in tropical soils. If the threshold effects observed here are widespread, they may pose greater challenges to mitigating NO emissions especially when (as in Tumbi) thresholds occurred at fertilization levels that were insufficient for achieving adequate crop productivity.

We did not measure NH₃ emissions. Zheng et al. [\(2019a](#page-21-8)) observed extremely high rates of NH₃ emissions in sandy soils in Tumbi, Tanzania—77.6 kg N ha⁻¹ from plots fertilized with urea broadcast at 150 kg N ha⁻¹—but much lower emission rates at a site with clayey soils. However, they showed that placing the urea at 5 cm depth reduced emissions to near-background levels. In our plots, fertilizer was placed at roughly 2–5 cm depth at planting, and at roughly 2–3 cm depth at topdressing, which likely limited volatilization losses (Bittman et al., [2014;](#page-19-28) Recio et al., [2018](#page-20-30)).

4.4. Partial N Budgets

We expected N mining to occur when less than 75 kg N ha⁻¹ was applied. Although this pattern was generally followed in Tumbi, in Yala, however, more N was removed from the crop fields through harvest of grain, cores, stover, emissions of NO, N_2O , and leaching of NO_3^- than was added in fertilizer, leading to apparent nutrient mining even when fertilization rates were 2–3 times recommended rates, and before considering any unmeasured losses via soil erosion or emissions of NH₃ and N₂. These negative partial budgets were primarily the result of the high yields and associated high levels of N uptake, with at least 100 kg N ha⁻¹ removed in aboveground biomass N across the different treatments. Because we did not measure all possible loss pathways (e.g., N_2 , NH₃), our balances were conservative estimates and could, in fact, be more negative. Nitrogen removal in maize biomass comprised roughly 84% of the total N losses but leaching fluxes also made an important contribution to the partial N budget (about 16% of total N losses). Our results were similar to those of Zheng, Kilasara, et al. ([2018\)](#page-21-4), Zheng, Mmari, et al. ([2018\)](#page-21-7), and Zheng et al. ([2019a,](#page-21-8) [2019b\)](#page-21-3) for clayey soils in Tanzania who found negative N budgets except in plots receiving 150 kg N ha⁻¹ and where NO_3^- leaching comprised about 99% of total N losses (Table S4 in Supporting Information S1).

Nutrient mining is widespread across SSA but is typically associated with low levels of mineral fertilizer inputs (FAO, [2022](#page-19-29); Henao & Baanante, [1999](#page-19-30); Olupot et al., [2021](#page-20-31)). Our results show the potential for N mining to occur even at higher rates of N fertilizer application. Although N mining at higher fertilization is not commonly reported, it can occur when yields are high (Rawal et al., [2022](#page-20-32)). Based on our findings, recommended rates of N fertilization for Yala of 58 kg N ha−1 year for western Kenya (FarmLink, [2018\)](#page-19-31) result in N mining. This suggests that in East African soils with higher productivity potential, recommended fertilizer applications may not be sufficient to prevent nutrient mining. Adopting management practices that increase N application rates with high crop demand, synchronize applications with crop growth, and combine fertilizer with organic inputs that can slow overall release and availability of N (Palm et al., [2001\)](#page-20-33) will be important for increasing yields, sustaining soil N balances, and limiting N losses.

In Tumbi, partial N balances followed our expected pattern where partial budgets were slightly negative when <50 kg N ha−1 was added, but roughly balanced or were positive at higher rates of fertilization. However, this

may have only occurred because Tumbi was a much less productive site than Yala. The recommended rate of 80 kg N ha−1 (very similar to our 75 kg N ha−1) will likely result in a roughly balanced N budget, with substantial increases in yields, and modest increases in N_2O and NO_3^- losses over the controls. It must be emphasized that these yields of less than 3 tons ha⁻¹ were still low in absolute terms. If $NO₃⁻$ losses were considered on a per unit production basis, they would be larger in Tumbi than Yala, and the same is true to an even greater extent for N2O and NO, particularly in the first year.

5. Implications and Conclusions

Despite large differences in soil texture and annual rainfall, maize N uptake at both Yala and Tumbi plateaued at fertilizer rates of 100 kg N ha−1 yr−1. However, yields were about two to five times higher in Yala than Tumbi, which led to substantial differences in partial N budgets. We suggest that fertilizer rates need not exceed 100 kg N ha⁻¹ yr⁻¹ at either site to meet crop yield goals and minimize losses through leaching and NO or N₂O emissions. Some nutrient mining will occur in Yala even at this level of N input. We studied only short-term N additions to soils not previously receiving continuous N additions and it is possible that greater annual N additions could increase N losses over time.

The two sites represented very different soil textural and climate regimes. Fluid transport, as mediated by rainfall and soil permeability, appears to be a first-order control over the magnitude of NO₃⁻-N leaching in Yala where N leaching losses were much higher in 2012 than 2013 because of higher precipitation during the growing season. Although NO and $N₂O$ emissions were low and should not be a primary concern for smallholder farmers, the non-linear relationships between emissions and N inputs suggest that threshold effects should be considered if managing these emissions becomes a priority on the future. Our detailed N budgets in two contrasting maize systems in East Africa highlight the challenges that smallholders face in increasing food production while limiting losses that diminish the benefits derived from the costly investment in fertilizers. In the most vulnerable places with the least and most variable rainfall, such as Tumbi, such mismatches between maize growth and fertilizer applications are more likely to occur. Climate change is expected to alter rainfall regimes across SSA, which will have impacts on agricultural yields and the fate of applied fertilizer because both leaching and gaseous losses are tied to water content and movement through soil profiles. Improving practices that optimize crop yields and minimize fertilizer losses will depend on the interactions of soil texture, the magnitude and timing of precipitation, and understanding of how those will change in a future climate across a wide range of soil and climate conditions.

Global Research Collaboration

This study was conceived and conducted in Kenya and Tanzania as part of the Millennium Villages Project (MVP), a multidimensional project in 10 African nations designed to accelerate community-based implementation of the United Nations Millennium Development Goals using targeted interventions to improve food production, health, and infrastructure. This research project was conducted in partnership with MVP staff based in Sauri, Kenya and Mbola, Tanzania and focused on ways of improving food production. Partial funding for the project was provided by a National Science Foundation Partnership for International Research and Education program grant to CN and CP to work with collaborators based at Kenyan and Tanzanian academic and governmental institutions. MVP staff collaborated on the experimental design, implementation, data collection, data interpretation, and final manuscript preparation. Templates for data collection and input were used by scientific leaders and data managers from each site. The results were shared with their local and national collaborators, in addition to the MVP team in the US and the MVP regional center in Nairobi, Kenya.

Data Availability Statement

Data from field measurements in Yala, Kenya and Tumbi, Tanzania of maize yields, soil solution N concentrations, NO₃⁻ leaching fluxes, N gas fluxes, ¹⁵N in maize tissues and soil, rainfall and temperature reported in the study are available at Dryad [\(www.datadryad.org\)](http://www.datadryad.org/) via <https://doi.org/10.5061/dryad.rxwdbrvcj> under a [CC 1.0 \(CC0 1.0\) Public Domain Dedication](https://creativecommons.org/publicdomain/zero/1.0/) license.

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